

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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Title: SLIDABLY MOVABLE MEMBER  
AND METHOD OF PRODUCING  
SAME

Appl. No.: Unassigned

Filing Date: April 7, 2000

Examiner: Unassigned

Art Unit: Unassigned

**UTILITY PATENT APPLICATION**  
**TRANSMITTAL**

Assistant Commissioner for Patents  
Box PATENT APPLICATION  
Washington, D.C. 20231

Sir:

Transmitted herewith for filing under 37 C.F.R. § 1.53(b) is the nonprovisional utility patent application of:

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Enclosed are:

- [ X ] Specification, Claim(s), and Abstract (22 pages).
- [ X ] Formal drawings (3 sheets, Figures 1-5).
- [ X ] Unexecuted Declaration and Power of Attorney (4 pages).
- [ X ] Claim for Convention Priority and certified copy of priority document.

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				SUBTOTAL:	= \$924.00
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## SLIDABLY MOVABLE MEMBER AND METHOD OF PRODUCING SAME

### BACKGROUND OF THE INVENTION

5 This invention relates to improvements in a slidably movable member having a hard carbon-based film which is low in friction, and more particularly to the slidably movable member having the hard carbon-based film suitable to be used in a condition to be in contact with engine lubricating oil, transmission oil or the  
10 like.

Hitherto, formation of hard carbon-based films have been proposed and put into practical use. The hard carbon-based films are formed of carbon-based materials such as amorphous carbon (a-C), a hydrogen-containing amorphous carbon (a-C:H), i-carbon (i-C) and  
15 diamond like carbon (DLC). The carbon-based films are usually formed by a plasma enhanced chemical vapor deposition (CVD) process in which hydrocarbon gas is plasma-decomposed to form the carbon-based film, or by an ion beam vapor deposition process using carbon and hydrocarbon ions. The thus formed carbon-based film  
20 has a high surface hardness and a high surface smoothness, and a high wear-resistance. Additionally, the carbon-based film is low in friction coefficient owing to solid lubricating characteristics, thereby exhibiting a low friction characteristics. The carbon-based film has a friction coefficient of about 0.1 under the condition of no lubrication, whereas a normal steel having a smooth surface has a friction  
25 coefficient ranging from 0.5 to 1.0 under the condition of no lubrication.

The hard carbon-based films have been presently applied to slidably movable members or parts to be used in a condition of no  
30 lubrication, for example, cutting tools such as a blade of a drill, processing jigs for the cutting tool, metal dies for plastic working, valve cocks and capstan rollers. Additionally, machine parts (such as those of an internal combustion engine) slidably movable in

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lubricating oil have been increasingly required to be reduced in mechanical loss from the viewpoints of energy saving and environmental protection. Particularly, such machine parts have been required to be lowered in friction by using the above-discussed  
5 hard carbon-based film having the solid lubricating characteristics in case that they are used in a section which is in a severe frictional condition causing a high friction loss.

#### SUMMARY OF THE INVENTION

In this regard, in case that a slidably movable member is  
10 coated with the above-mentioned hard carbon-based film and used to be slidably moved in engine lubricating oil, transmission oil or the like, a low friction characteristics can be obtained to some extent owing to the smoothness of the hard carbon-based film. However, it has been revealed, as a problem, that the slidably movable member  
15 coated with the hard carbon-based film is generally equal in low friction characteristics to other slidably movable members coated with hard films having no solid lubricating characteristics, such as those formed by ion plating of titanium nitride (TiN) or chromium nitride (CrN). In other words, it has been revealed, as a problem,  
20 that the slidably movable member coated with the conventional carbon-based film is generally equal in low friction characteristics in lubricating oil to slidably movable members coated with the film having no solid lubricating characteristics and the generally same surface roughness, or to superfinished steel members, even though  
25 they coated with the conventional carbon-based film have the solid lubricating characteristics.

More specifically, for example, when three steel balls having a 3/8 inch diameter are pushed onto the hard carbon-based film of diamond like carbon under a load of 1 kgf in lubricating oil  
30 and slid at a relative speed of 0.03 m/sec., the hard-carbon based film of diamond like carbon exhibits a friction coefficient ranging from 0.08 to 0.12 which is the generally same as that of the ion-plated chromium nitride (CrN) film or that of a steel material having the

generally same surface roughness and provided with no hard coating treatment.

In addition, slidably movable members or parts coated with molybdenum disulfide ( $\text{MoS}_2$ ) or polytetrafluoroethylene (PTFE) having solid lubricating characteristics have been put into  
5 practical use in order to realize a low friction characteristics having a friction coefficient  $\mu$  lower than 0.07 in lubricating oil such as engine lubricating oil or transmission oil. However, in case that such conventional slidably movable members or parts are used in further  
10 severe conditions and under a high bearing pressure, they are insufficient in wear resistance so that a necessary performance of wear resistance may be achieved only at an initial period in service but cannot be maintained for a long period of time in service.

It is an object of the present invention to provide an  
15 improved slidably movable member which can effectively overcome drawbacks encountered in conventional slidably movable members which are used in contact with lubricating oil.

Another object of the present invention is to provide an improved slidably movable member which is high in wear resistance  
20 even in a condition to be in contact with lubricating oil, throughout a long period of time in service.

A further object of the present invention is to provide an improved slidably movable member whose solid lubricating characteristics is effective even in lubricating oil so as to exhibit a  
25 low friction characteristics having a friction coefficient  $\mu$  of not higher than 0.07.

A first aspect of the present invention resides in a slidably movable member used in contact with lubricating oil. The slidably movable member comprises a substrate. A hard carbon-based film is  
30 coated on a surface of the substrate. The hard carbon-based film has a surface section which contains at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at%.

5 A second aspect of the present invention resides in an adjusting shim used in a valve operating mechanism of an internal combustion engine. The adjusting shim comprises a substrate. A hard carbon-based film is coated on a surface of the substrate. The hard carbon-based film has a surface section which contains at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at%.

10 A third aspect of the present invention resides in a slidably movable member used in contact with lubricating oil. The slidably movable member comprises a substrate. A hard carbon-based film is coated on a surface of the substrate. The hard carbon-based film having a surface section which contains hydrogen in an amount of not more than 10 at%.

15 A fourth aspect of the present invention resides in a slidably movable member used in contact with lubricating oil. The slidably movable member comprises a substrate. A hard carbon-based film is coated on a surface of the substrate. The hard carbon-based film having a surface section which contains at least one of nitrogen in an amount ranging from 0.5 to 30 at%, oxygen in an amount ranging from 0.5 to 30 at%, and hydrogen in an amount of  
20 not more than 10 at%.

25 A fifth aspect of the present invention resides in a method of producing a slidably movable member used in contact with lubricating oil. The producing method comprises (a) preparing a substrate; (b) coating a hard carbon-based film on a surface of the substrate by a chemical vapor deposition process; and (c) causing a surface section of the hard carbon-based film to contain at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at% by one of a plasma treatment and an ion implantation process.

30 A sixth aspect of the present invention resides in a method of producing a slidably movable member used in contact with lubricating oil. The producing method comprises (a) preparing a substrate; and (b) coating a hard carbon-based film on a surface of the substrate by one of a carbon ion beam process, a thermal

chemical vapor deposition process, an ion plating process, and a sputtering process, to cause a content of hydrogen in a surface section of the hard carbon-based film to fall within a range of not more than 10 at%.

5 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an explanatory perspective view of an embodiment (adjusting shim) of a slidably movable member according to the present invention;

10 Fig. 2 is an explanatory sectional view of a plasma treatment apparatus used for accomplishing a plasma treatment on a hard carbon-based film formed on a substrate, so as to produce the slidably movable member according to the present invention;

15 Fig. 3 is an explanatory sectional view of a friction tester for measuring a coefficient of friction of the slidably movable member according to the present invention;

Fig. 4 is a fragmentary explanatory sectional view of an essential part of a valve operating mechanism of an internal combustion engine, in which the slidably movable member according to the present invention is used as an adjusting shim; and

20 Fig. 5 is a graph showing test results of measurement of a friction loss torque, obtained by using the valve operating mechanism of Fig. 4.

DETAILED DESCRIPTION OF THE INVENTION

25 According to the present invention, a slidably movable member used in contact with lubricating oil comprises a substrate. Additionally, a hard carbon-based film is coated on a surface of the substrate. The hard carbon-based film is a film whose main component is carbon. The hard carbon-based film has a surface section which contains at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at% (atomic percent) and/or hydrogen

30 in an amount of not more than 10 at%. The surface section of the hard carbon-based film includes a surface of the hard carbon-based film. More specifically, the hard carbon-based film has a thickness

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ranging from 1 to 10  $\mu\text{m}$ , in which the thickness of the surface section is 1/10 of that of the surface section. Accordingly, at least the surface section of the hard carbon-based film contains nitrogen and/or oxygen in the above-mentioned amount. It will be understood that nitrogen and/or oxygen may be contained in the above-mentioned amount in the hard carbon-based film other than the surface section.

In the thus arranged slidably movable member having hard carbon-based film whose surface section contains at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at%, a large amount of polar groups are present at the surface of the hard carbon-based film, and therefore oiliness agents contained in lubricating oil are liable to be physically or chemically adsorbed at the surface of the hard carbon-based film. As a result, a low friction characteristics can be provided to the hard carbon-based film so that the hard carbon-based film exhibits a low coefficient of friction  $\mu$  of not higher than 0.07. In this regard, if the content (amount) of nitrogen and/or oxygen in the surface section of the hard carbon-based film is less than 0.5 at%, there is a tendency that the above-mentioned low friction characteristics in lubricating oil cannot be realized. In contrast, if the content exceeds 30 at%, wear resistance under a high bearing pressure is insufficient. Preferably, the content of nitrogen and/or oxygen is within a range of from 4 to 20 at%, which effectively provides a low friction characteristics in lubricating oil without degrading a wear resistance and a smoothness of the hard carbon-based film. The content of nitrogen and/or oxygen is measured by a X-ray photoelectron spectra (XPS) "ESCA-5600" produced by PHI (Physical Electronics, Inc.).

The slidably movable member is produced by a method comprising (a) preparing a substrate; (b) coating a hard carbon-based film on a surface of the substrate by a chemical vapor deposition process; and (c) causing a surface section of the hard carbon-based film to contain at least one of nitrogen and oxygen in



an amount ranging from 0.5 to 30 at% by one of a plasma treatment and an ion implantation process.

Under a plasma treatment, nitrogen and/or oxygen are supplied to be contained in the surface section of the hard carbon-based film. The plasma treatment is carried out by using a plasma treatment apparatus 21 as shown in Fig. 2. The plasma treatment apparatus 21 includes a vacuum vessel 22. A substrate holder 24 is disposed inside the vacuum vessel 22 and located at a lower position in order to support the substrate (coated with the hard carbon-based film) 23 constituting the slidably movable member 1. The substrate holder 24 is electrically connected to a bias power source 25. RF electrodes 26 are provided above the substrate holder 24 and electrically connected to a RF power source 27.

A plasma forming gas contained in a gas bomb 28 is supplied through a gas regulator 29 to the RF electrodes 26 each having a central opening 26a, so that plasma is formed between the electrodes 26 under RF discharge. Then, ion 32 is formed in an aperture electrode 31 so that radical ion beam 33 reaches the surface section of the hard carbon-based film formed at the surface of the substrate 23. Consequently, the plasma forming gas is contained in the surface section of the hard carbon-based film. Evacuation of the vacuum vessel 22 is accomplished in a direction indicated by an arrow A by an evacuator (not shown). Such a plasma treatment is accomplished, for example, under a condition where a RF input power is within a range of from 10 to 100 W; a flow rate of the plasma forming gas is within a range of from 5 to 50 cc/min.; and a bias voltage applied from the bias power source 25 is within a range of from -250 to +250 V.

While the plasma treatment has been discussed to cause the surface section of the hard carbon-based film to contain nitrogen and/or oxygen, it will be understood that an ion implantation may be used for the same purpose.

Otherwise, the low friction characteristics in lubricating oil can be obtained by controlling the content or concentration of hydrogen at a level of not more than 10 at% in the surface section of the hard carbon-based film. Although measurement of content of hydrogen in the surface section is difficult, the content can be readily estimated from conditions where formation of the hard carbon-based film is accomplished. Accordingly, such a low content of hydrogen can be realized by forming the hard carbon-based film of amorphous carbon by a carbon ion beam process or the like in which hydrocarbon plasma is not used at least during formation of the hard carbon-based film, or by forming the hard carbon-based film of a diamond polycrystal by a thermal chemical vapor deposition (CVD) process. Additionally, such a low content of hydrogen can be realized by forming the hard carbon-based film by an ion plating process, or by a sputtering process. With the thus formed hard carbon-based film, a large amount of polar groups are present at the surface of the hard carbon-based film, and therefore oiliness agents contained in lubricating oil are liable to be physically or chemically adsorbed at the surface of the hard carbon-based film. It will be understood that hydrogen may be contained in the above-mentioned amount in the hard carbon-based film other than the surface section.

Further, it is preferable that the hard carbon-based film has a surface roughness Ra of not higher than 0.1  $\mu\text{m}$ , so that the hard carbon-based film can have a low friction characteristics and a low aggressivity against an opposite member to which the slidably movable member is contacted. The surface roughness Ra is measured according to JIS (Japanese Industrial Standard) B 0601. Additionally, it is also preferable that the hard carbon-based film has a surface hardness Hv (by Vickers hardness test according to JIS Z 2244) of not lower than 1000. It is also preferable that the hard carbon-based film has a thickness ranging from 1 to 10  $\mu\text{m}$ . If the thickness is lower than 1  $\mu\text{m}$ , the hard carbon-based film is insufficient in adherence strength. If the thickness exceeds 10  $\mu\text{m}$ ,

residual stress in the hard carbon-based film is high so that the hard carbon-based film may naturally peel off. The thickness of the hard carbon-based film is microscopically measured.

5 The slidably movable member 1 is preferably used as an adjusting shim in the form shown in Fig. 1. The adjusting shim is, for example, mounted on a valve lifter for an engine valve (intake or exhaust valve) of an internal combustion engine of an automotive vehicle. The valve lifter forms part of a valve operating mechanism for operating the engine valve under drive of the engine. The  
10 adjusting shim is in slidable contact with a camshaft in a condition to be coated with lubricating oil. The adjusting shim functions to adjust a valve clearance of the engine valve.

#### EXAMPLES

The present invention will be more readily understood  
15 with reference to the following Examples in comparison with Comparative Examples; however, these Examples are intended to illustrate the invention and are not to be construed to limit the scope of the invention.

#### EXAMPLE 1

20 First, a disc-shaped substrate 2 made of ceramic (silicon nitride) was prepared to have a dimension of a 30 mm diameter and a 4 mm thickness, as shown in Fig. 1. A diamond polycrystal film (synthesized in gas phase) having a thickness of 10.0  $\mu\text{m}$  was deposited on an upper surface of the substrate 2 by a thermal CVD  
25 process to form a hard carbon-based film 3 as shown in Fig. 1. The surface section of the hard carbon-based film 3 was estimated to contain hydrogen in an amount less than 10 at%. Subsequently, the surface of the diamond polycrystal film or hard carbon-based film 3 was ground to be finished by a diamond wheel or abrasive grain  
30 thereby obtaining a surface roughness Ra of 0.05  $\mu\text{m}$ . As a result, a slidably movable member 1 as shown in Fig. 1 was produced.

#### EXAMPLE 2

First, a disc-shaped substrate 2 made of carburized steel (SCM415, chromium molybdenum steel, according to JIS G 4105) was prepared to have a dimension of a 30 mm diameter and a 4 mm thickness, as shown in Fig. 1. A super finishing was made on the upper surface of the substrate 2 to have a surface roughness Ra of 0.04  $\mu\text{m}$ . Thereafter, a hard carbon-based film 3 was coated on the upper surface of the substrate 2 by an ion plating process using carbon ion beam, as shown in Fig. 1. The surface section of the hard carbon-based film 3 was estimated to contain hydrogen in an amount less than 10 at%. As a result, a slidably movable member 1 as shown in Fig. 1 was produced to have a surface roughness Ra of 0.09  $\mu\text{m}$  without being subjected to finishing after formation of the hard carbon-based film 3.

#### EXAMPLE 3

A slidably movable member 1 of Example 3 was produced similarly to Example 2 with the exception that lapping was made on the upper surface of the slidably movable member 1 so that the slidably movable member has a surface roughness Ra of 0.03  $\mu\text{m}$ .

#### EXAMPLE 4

First, a disc-shaped substrate 2 made of carburized steel (according to JIS SCM415) was prepared to have a dimension of a 30 mm diameter and a 4 mm thickness, as shown in Fig. 1. A super finishing was made on the upper surface of the substrate 2 to have a surface roughness Ra of 0.04  $\mu\text{m}$ . Thereafter, a diamond like carbon (DLC) film or hard carbon-based film 3 was formed on the upper surface of the substrate 2 by a plasma enhanced CVD process using hydrocarbon gas. The surface section of the hard carbon-based film 3 was estimated to contain hydrogen in an amount more than 10 at%. Subsequently, the substrate 2 with the DLC film was put on the substrate holder 24 in the plasma treatment apparatus 21 and subjected to an oxygen plasma treatment to cause the surface section of the hard carbon-based film 3 to contain oxygen under the following conditions: the RF input power was 50 W; the oxygen gas

flow rate was 10 cc/min.; and the bias voltage was -100 V. As a result, a slidably movable member 1 as shown in Fig. 1 was produced to have the hard carbon-based film whose the surface section had an oxygen content of about 3.5 at%.

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## EXAMPLE 5

The slidably movable member 1 of Example 3 was put on the substrate holder 24 in the plasma treatment apparatus 21 and subjected to an oxygen plasma treatment similar to that in Example 4. The hard carbon-based film 3 was estimated to contain hydrogen in an amount less than 10 at%. As a result, a slidably movable member 1 as shown in Fig. 1 was produced to have the hard carbon-based film whose surface section had an oxygen content of about 3.5 at%.

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## EXAMPLE 6

The slidably movable member 1 of Example 1 was put on the substrate holder 24 in the plasma treatment apparatus 21 so that the diamond polycrystal film or hard carbon-based film 3 was subjected to a nitrogen plasma treatment to cause the surface section of the hard carbon-based film 3 to contain nitrogen, under conditions similar to those in Examples 4 and 5 with the exception that the oxygen gas flow rate was replaced with a nitrogen gas flow rate. The hard carbon-based film 3 was estimated to contain hydrogen in an amount less than 10 at%. As a result, a slidably movable member 1 of Example 6 was produced to have the hard carbon-based film 3 whose surface section had a nitrogen content of about 5.7 at%, as shown in Fig. 1.

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## COMPARATIVE EXAMPLE 1

First, a disc-shaped substrate made of carburized steel (according to JIS SCM415) was prepared to have a dimension of a 30 mm diameter and a 4 mm thickness, as shown in Fig. 1. Grinding was made on the upper surface of the substrate to have a surface roughness Ra of 0.24  $\mu\text{m}$ . Thereafter, the upper surface of the substrate 2 was subjected to a manganese phosphate treatment for

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forming a manganese phosphate coating. As a result, a slidably movable member of Comparative Example 1 as shown in Fig. 1 was produced.

#### COMPARATIVE EXAMPLE 2

- 5 First, a disc-shaped substrate 2 made of carburized steel (according to JIS SCM415) was prepared to have dimensions of a 30 mm diameter and a 4 mm thickness, as shown in Fig. 1. Thereafter, super finishing was made on the upper surface of the substrate 2 to have a surface roughness Ra of 0.04  $\mu\text{m}$ . As a result, a slidably movable member of Comparative Example 2 like that as shown in Fig. 1 was produced.

#### COMPARATIVE EXAMPLE 3

- 15 The slidably movable member of Comparative Example 2 was subjected to an ion plating process, in which the surface of the slidably movable member was coated with chromium nitride (CrN). As a result, a slidably movable member of Comparative Example 3 as shown in Fig. 1 was produced to have a chromium nitride film having a thickness of 2.0  $\mu\text{m}$  and a surface hardness Hv of 1500.

#### COMPARATIVE EXAMPLE 4

- 20 First, a disc-shaped substrate made of ceramic (silicon nitride) was prepared to have a dimension of a 30 mm diameter and a 4 mm thickness, as shown in Fig. 1. A diamond polycrystal film (synthesized in gas phase) having a thickness of 10.0  $\mu\text{m}$  was deposited on an upper surface of the substrate by a thermal CVD process to form a hard carbon-based film like that as shown in Fig. 1. The hard carbon-based film 3 was estimated to contain hydrogen in an amount less than 10 at%. As a result, a slidably movable member of Comparative Example 4 as shown in Fig. 1 was produced to have a surface roughness Ra of 0.12  $\mu\text{m}$ .

- 30 COMPARATIVE EXAMPLE 5

First, a disc-shaped substrate made of carburized steel (according to JIS SCM415) was prepared to have a dimension of a 30 mm diameter and a 4 mm thickness, as shown in Fig. 1. Then, super

finishing was made on the upper surface of the substrate to have a surface roughness Ra of 0.04  $\mu\text{m}$ . Thereafter, a diamond like carbon (DLC) film was formed on the upper surface of the substrate by a plasma enhanced CVD process using hydrocarbon gas. The surface section of the hard carbon-based film was estimated to contain hydrogen in an amount more than 10 at%. As a result, a slidably movable member of Comparative Example 5 as shown in Fig. 1 was produced.

#### COMPARATIVE EXAMPLE 6

First, a disc-shaped substrate made of carburized steel (according to JIS SCM415) was prepared to have a dimension of a 30 mm diameter and a 4 mm thickness, as shown in Fig. 1. Grinding was made on the upper surface of the substrate to have a surface roughness Ra of 0.20  $\mu\text{m}$ . Thereafter, a hard carbon-based film was coated on the upper surface of the substrate by an ion plating process using carbon ion beam. The surface section of the hard carbon-based film was estimated to contain hydrogen in an amount less than 10 at%. As a result, a slidably movable member of Comparative Example 6 as shown in Fig. 1 was produced to have a surface roughness Ra of 0.25  $\mu\text{m}$ .

#### COMPARATIVE EXAMPLE 7

The slidably movable member of Comparative Example 6 was put on the substrate holder 24 in the plasma treatment apparatus 21 and subjected to an oxygen plasma treatment similar to that in Example 4. The surface section of the hard carbon-based film was estimated to contain hydrogen in an amount less than 10 at%. As a result, a slidably movable member of Comparative Example 7 as shown in Fig. 1 was produced to have the hard carbon-based film whose surface section had an oxygen content of about 40 at%.

The essential points of Examples and Comparative Examples are shown at the upper part of Table 1.

#### EXPERIMENT

In order to evaluate the performance of the slidably movable members according to the present invention, the coefficient of frictions of the slidably movable members were measured by using a pin-on-disc type friction tester 41 as shown in Fig. 3.

- 5           The friction tester 41 included a work table 43 which was rotatably supported through a rotatable shaft 42. Three steel balls 44 were fixedly supported by a ball holder 46, and located above the work table 43. Each steel ball 44 had a diameter of 3/8 inch and formed of a steel (SUSJ2, high carbon chromium bearing steel, according to JIS G 4805). A slidably movable member (of Examples and Comparative Examples) was securely mounted, as a test piece, on the work table 43, so that the steel balls 44 were in slidable contact with the slidably movable member 1. The steel balls 44 were pressed onto the slidably movable member 1 at a load of 1.0 kgf by a spring 45, through a spring support 46a connected to the ball holder 46. The rotatable shaft 42 was directly connected to a motor 47 and rotated at a relative sliding speed ranging from 0.01 to 0.1 m/sec. to the steel balls 44. A load cell 48 was connected to the spring support 46a so as to measure a force due to a torque generated in accordance with a friction between the steel balls 44 and the slidably movable member 1. Additionally, an oil bath 50 was provided so that the slidably movable member 1 was able to be dipped in lubricating oil 49. The temperature of the lubricating oil 49 was controlled at about 80 °C by an oil temperature control unit (not shown). The lubricating oil was an engine lubricating oil (5W-30SG) available on the market. From the measured force due to the torque, a coefficient of friction  $\mu$  was calculated as shown in Table 1. In this experiment, two kinds of friction coefficients  $\mu$  were measured, in which one friction coefficient  $\mu$  was measured in the lubricating oil while the other friction coefficient  $\mu$  was measured without the lubricating oil (or under no lubrication) so that no lubricating oil was supplied in the oil bath 50, under the same conditions in which the load applied to
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the three balls 44 was 1 kgf; and the relative sliding speed was 0.25 m/sec (250 r.p.m.).

As apparent from the test result shown in Table 1, the hard carbon-base films of Examples have a solid lubricating characteristics, and therefore the slidably movable members of Examples are low in friction coefficient as compared with the slidably movable members of Comparative Example 2 having no hard film and of Comparative Examples 1 and 3 having the hard film having no solid lubricating characteristics, under the condition of no lubrication.

However, under the condition of lubrication using the lubricating oil, the slidably movable member of Comparative Example 5 having the hard film of diamond like carbon having a hydrogen content higher than 10 at% is generally equivalent in friction coefficient to the slidably movable members of Comparative Examples 1 and 2 having no hard film. The friction coefficient is higher than 0.07 and therefore low in friction lowering effect even in the slidably movable member of Comparative Example 4 having the hard film of diamond polycrystal film (or amorphous carbon film) in case that the surface roughness Ra of the slidably movable member is over 0.10  $\mu\text{m}$ .

In contrast, the slidably movable members of Examples 1 to 6 have a friction coefficient of not higher than 0.07. These slidably movable members are provided with the hard films having a hydrogen content lower than 10 at% and/or a specified nitrogen or oxygen content and having a surface roughness Ra of not higher than 0.01  $\mu\text{m}$ . This reveals that these slidably movable members can be effectively lowered in friction loss even in lubricating oil.

Furthermore, a friction loss torque (torque corresponding to a friction loss) was measured for a cam of a camshaft of a valve operating mechanism of an internal combustion engine in case that the slidably movable members of Example 5 and Comparative

Examples 1, 2, 3 and 5 was used as an adjusting shim, by using the engine having the valve operating mechanism shown in Fig. 4.

In the valve operating mechanism shown in Fig. 4, the camshaft 52 having cams 51 was driven to rotate through a timing belt by the engine. An engine (intake or exhaust) valve 53 was slidably inserted in a valve guide 54. A valve lifter 55 was disposed at an upper end of the valve 53. A valve spring 57 was disposed between the valve lifter 55 and a cylinder head 56. The upper end section of the valve spring 57 is fixed to a stem section of the valve 53 by using a retainer 58 and a cotter 59. The valve spring 57 functioned to apply load to the valve 53 in a direction in which the valve 53 closes. The adjusting shim 60 was fitted in a depression formed at the top section of the valve lifter 55 and had such a thickness that a clearance of about 0.3 mm was formed between the cam 51 and the adjusting shim 60. Upon rotation of the camshaft 52, the cam 51 rotated and was in slidable contact with the adjusting shim 60 thereby making reciprocating movement of the valve 53.

The camshaft 52 was driven by a motor (not shown) through a torque meter (not shown) installed on an end section of the camshaft to measure a torque corresponding to a friction loss generated between the cam 51 and the adjusting shim 60, under the following conditions: A rotational speed of the camshaft 52 was 3000 r.p.m. (corresponding to idling); a maximum load of the valve spring 57 was 50 kgf; an engine lubricating oil temperature was 80 °C; the cam 51 to which the adjusting shim 60 was slidably contacted had been subjected to superfinishing so as to have a surface roughness Ra of 0.05  $\mu\text{m}$ . The result of measurement of the friction loss torque is shown in the form of a bar graph in Fig. 5 in which bars a, b, c, d and e respectively represent Example 5 (1.64 kg-cm), Comparative Example 1 (2.87 kg-cm), Comparative Example 2 (2.40 kg-cm), Comparative Example 3 (2.43 kg-cm) and Comparative Example 5 (2.28 kg-cm).

As apparent from Fig. 5, the slidably movable member of Example is low in friction loss torque as compared with that of Comparative Examples even in case having the same surface roughness. This reveals that the slidably movable member according to the present invention is high in friction performance.

The entire contents of Japanese Patent Application P11-102205 (filed April 9, 1999) are incorporated herein by reference.

Although the invention has been described above by reference to certain embodiments of the invention, the invention is not limited to the embodiments described above. Modifications and variations of the embodiments described above will occur to those skilled in the art, in light of the above teachings. The scope of the invention is defined with reference to the following claims.

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TABLE 1

Item	Substrate	Hard film	Film forming process	Thickness (μm)	Hardness (Hv)
Example	1 Silicon nitride	Diamond polycrystal film	Thermal CVD	10.0	-
	2 Carburized steel	Hard carbon-based film (a-C)	Ion plating	2.0	3500
	3 Carburized steel	Hard carbon-based film (a-C)	Ion plating	2.0	3500
	4 Carburized steel	DLC film	Plasma enhanced CVD	1.0	2500
	5 Carburized steel	Hard carbon-based film (a-C)	Ion plating	2.0	3500
	6 Silicon nitride	Diamond polycrystal film	Thermal CVD	10.0	-
Compar. Example	1 Carburized steel	Manganese phosphate film	Chemical treatment	10.0	-
	2 Carburized steel	None	-	-	720
	3 Carburized steel	CrN film	Ion plating	2.0	1500
	4 Carburized steel	Diamond polycrystal film	Thermal CVD	10.0	-
	5 Carburized steel	DLC film	Plasma enhanced CVD	1.0	2500
	6 Carburized steel	Hard carbon-based film (a-C)	Ion plating	2.0	3500
	7 Carburized steel	Hard carbon-based film (a-C)	Ion plating	2.0	3500

	Surface roughness Ra (μm)	Reference	Friction coefficient μ		Item
			No lubrication	In lubricating oil	
Example	0.05	10 at% > hydrogen	0.080	0.058	1
	0.09	10 at% > hydrogen	0.110	0.065	2
	0.03	10 at% > hydrogen	0.090	0.066	3
	0.04	Oxygen plasma treatment, 3.5 at% oxygen, 10 at% < hydrogen	0.098	0.056	4
	0.04	Oxygen plasma treatment, 3.5 at% oxygen, 10 at% > hydrogen	0.095	0.059	5
	0.05	Nitrogen plasma treatment, 5.7 at% nitrogen, 10 at% > hydrogen	0.080	0.049	6
Compar. Example	1.50	-	1.080	0.125	1
	0.04	-	0.480	0.096	2
	0.07	-	0.380	0.108	3
	0.12	10 at% > hydrogen	0.090	0.075	4
	0.04	10 at% < hydrogen	0.098	0.099	5
	0.25	10 at% > hydrogen	0.125	0.085	6
	0.05	Oxygen plasma treatment, 40 at% oxygen, 10 at% > hydrogen	Peeled off	0.100	7

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## WHAT IS CLAIMED IS:

1. A slidably movable member used in contact with lubricating oil, comprising:  
a substrate; and  
5 a hard carbon-based film coated on a surface of said substrate, said hard carbon-based film having a surface section which contains at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at%.
- 10 2. A slidably movable member as claimed in Claim 1, wherein said hard carbon-based film is a diamond film formed by a chemical vapor deposition process.
3. A slidably movable member as claimed in Claim 1,  
15 wherein the surface section of said hard carbon-based film contains at least one of nitrogen and oxygen in an amount ranging from 4 to 20 at%.
4. A slidably movable member as claimed in Claim 1,  
20 wherein said hard carbon-based film has a surface roughness lower than 0.1  $\mu\text{m}$ .
5. A slidably movable member as claimed in Claim 1,  
25 wherein said hard carbon-based film has a hardness Hv higher than 1000.
6. A slidably movable member as claimed in Claim 1, wherein said hard carbon-based film has a thickness ranging from 1 to 10  $\mu\text{m}$ , wherein said hard carbon-based film has a coefficient of  
30 friction of not higher than 0.07 in a condition where said hard carbon-based film is dipped in a lubricating oil.

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7. A slidably movable member as claimed in Claim 1, wherein said substrate is formed of a material selected from the group consisting of silicon nitride and steel.
- 5 8. A slidably movable member as claimed in Claim 1, wherein said hard carbon-based film is formed of a material selected from the group consisting of diamond polycrystal, amorphous carbon, and diamond like carbon.
- 10 9. An adjusting shim used in a valve operating mechanism of an internal combustion engine, comprising:  
a substrate; and  
a hard carbon-based film coated on a surface of said substrate, said hard carbon-based film having a surface section  
15 which contains at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at%.
10. A slidably movable member used in contact with lubricating oil, comprising  
20 a substrate; and  
a hard carbon-based film coated on a surface of said substrate, said hard carbon-based film having a surface section which contains hydrogen in an amount of not more than 10 at%.
- 25 11. A slidably movable member as claimed in Claim 1, wherein said hard carbon-based film is formed by one of a carbon ion beam process, a thermal chemical vapor deposition process, an ion plating process, and a sputtering process.
- 30 12. A slidably movable member used in contact with lubricating oil, comprising:  
a substrate; and

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5 a hard carbon-based film coated on a surface of said substrate, said hard carbon-based film having a surface section which contains at least one of nitrogen in an amount ranging from 0.5 to 30 at%, oxygen in an amount ranging from 0.5 to 30 at%, and hydrogen in an amount of not more than 10 at%.

13. A method of producing a slidably movable member used in contact with lubricating oil, comprising:  
preparing a substrate;  
10 coating a hard carbon-based film on a surface of the substrate by a chemical vapor deposition process; and  
causing a surface section of the hard carbon-based film to contain at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at% by one of a plasma treatment and an ion  
15 implantation process.

14. A method of producing a slidably movable member used in contact with lubricating oil, comprising:  
preparing a substrate; and  
20 coating a hard carbon-based film on a surface of the substrate by one of a carbon ion beam process, a thermal chemical vapor deposition process, an ion plating process, and a sputtering process, to cause a content of hydrogen in a surface section of the hard carbon-based film to fall within a range of not more than 10  
25 at%.

ABSTRACT OF THE DISCLOSURE

A slidably movable member such as an adjusting shim used in a valve operating mechanism of an internal combustion engine of an automotive vehicle. The slidably movable member is used in contact with lubricating oil and comprises a substrate. A hard carbon-based film is coated on a surface of the substrate. The hard carbon-based film has a surface section which contains at least one of nitrogen and oxygen in an amount ranging from 0.5 to 30 at% and/or hydrogen in an amount of not more than 10 at%.

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FIG. 1

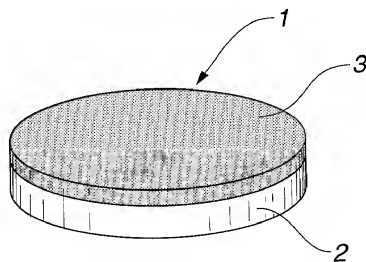
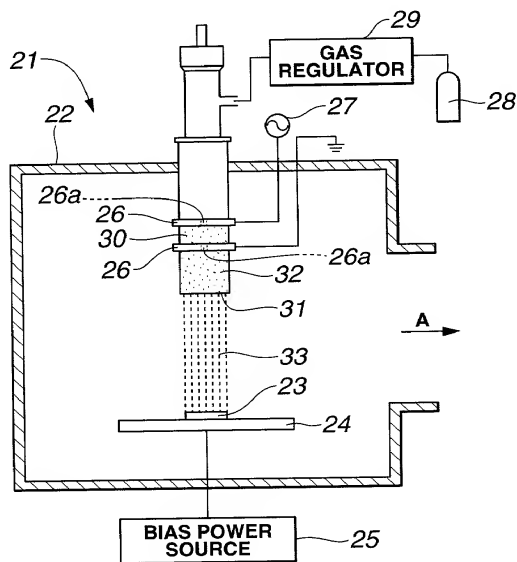
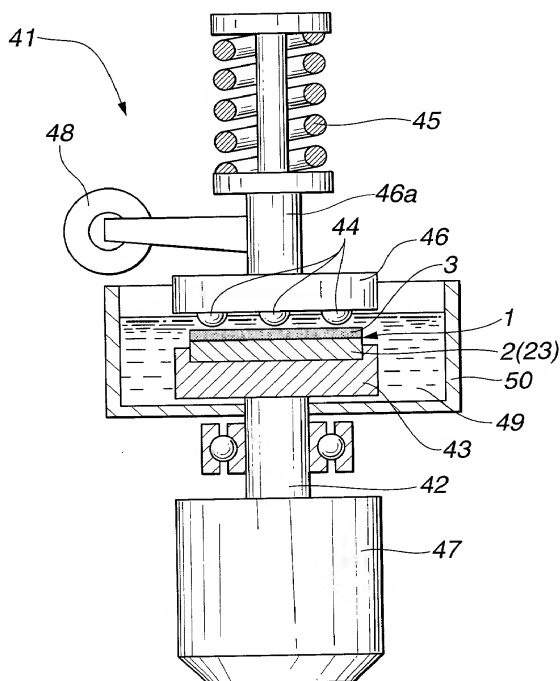


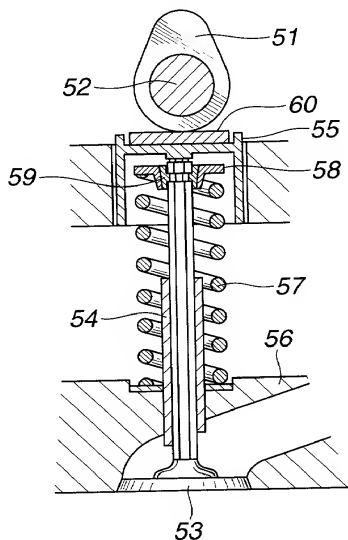
FIG. 2



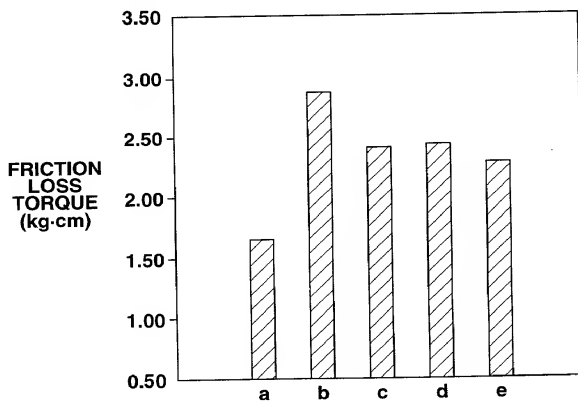
**FIG.3**



# FIG.4



# FIG.5



**DECLARATION AND POWER OF ATTORNEY**

As a below named inventor, I HEREBY DECLARE:

THAT my residence, post office address, and citizenship are as stated below next to my name;

THAT I believe I am the original, first, and sole inventor (if only one inventor is named below) or an original, first, and joint inventor (if plural inventors are named below or in an attached Declaration) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SLIDABLY MOVABLE MEMBER AND METHOD OF PRODUCING SAME

(Attorney Docket No. 040679/1047)

the specification of which (check one)

       is attached hereto.

  X   was filed on April 7, 2000 as United States Application Number or PCT International Application Number \_\_\_\_\_ and was amended on \_\_\_\_\_ (if applicable).

THAT I do not know and do not believe that the same invention was ever known or used by others in the United States of America, or was patented or described in any printed publication in any country, before I (we) invented it;

THAT I do not know and do not believe that the same invention was patented or described in any printed publication in any country, or in public use or on sale in the United States of America, for more than one year prior to the filing date of this United States application;

THAT I do not know and do not believe that the same invention was first patented or made the subject of an inventor's certificate that issued in any country foreign to the United States of America before the filing date of this United States application if the foreign application was filed by me (us), or by my (our) legal representatives or assigns, more than twelve months (six months for design patents) prior to the filing date of this United States application;

THAT I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment specifically referred to above;

THAT I believe that the above-identified specification contains a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the invention, and sets forth the best mode contemplated by me of carrying out the invention; and

THAT I acknowledge the duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I HEREBY CLAIM foreign priority benefits under Title 35, United States Code § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number	Country	Foreign Filing Date	Priority Claimed?	Certified Copy Attached?
11-102205	Japan	09 April 1999	Yes	

I HEREBY CLAIM the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

U.S. Provisional Application Number	Filing Date

I HEREBY CLAIM the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Application Number	Parent Filing Date	Parent Patent Number

I HEREBY APPOINT the following registered attorneys and agents of the law firm of FOLEY & LARDNER to have full power to prosecute this application and any continuations, divisions, reissues, and reexaminations thereof, to receive the patent, and to transact all business in the United States Patent and Trademark Office connected therewith:

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I UNDERSTAND AND AGREE THAT the foregoing attorneys and agents appointed by me to prosecute this application do not personally represent me or my legal interests, but instead represent the interests of the legal owner(s) of the invention described in this application.

I FURTHER DECLARE THAT all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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